PATENT SPECIFICATION (11) 1 397 245

1 397 245

(21) Application No. 38471/71 (22) Filed 17 Aug. 1971

(23) Complete Specification filed 16 Aug. 1972

(44) Complete Specification published 11 June 1975

(51) INT CL² C11D 3/60//(C11D 3/60, 1/02, 1/66, 1/88)

(52) Index at acceptance

C5D 6A5C 6A5E 6B10A 6B12A 6B12B1 6B12F1 6B12F2 6B12G2A 6B12G6 6B12N1 6B12N2 6B12P 6B1 6B8 6C6

(72) Inventor MALCOLM NIGEL ALAN CARTER

(19)

(54) DETERGENT COMPOSITIONS

(71) We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E.C.4, England, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to detergent compositions, and in particular to detergent compositions adapted for fabric washing.

Detergent compositions commonly incorporate as major ingredients detergent active compounds together with detergency builders. Conventional detergency builders are commonly inorganic materials, particularly the condensed phosphates, for example sodium tripolyphosphate. It has, however, been suggested that the use of phosphate detergency builders can contribute to eutrophication problems. Alternative detergency builders which have been proposed, for example sodium nitrilotriacetate (NTA) and synthetic polyelectrolyte materials, tend to be more expensive or less efficient than the phosphate detergency builders, or otherwise unsatisfactory for one reason or another.

It has been proposed to use sodium citrate and other weak sequestering agents as detergency builders, but these materials are not as efficient as would be desired when used to replace sodium tripolyphosphate in conventional detergent compositions.

We have now found that detergent compositions with salts of citric acid as detergency builders are improved by incorporating therein relatively high levels of certain detergent active compounds.

The invention provides a detergent composition comprising at least 20% by weight of a salt of citric acid detergency builder and either

(a) at least 15% by weight of a nonionic detergent active compound or a predominantly nonionic mixture of detergent active compounds; or

(b) from 25% to 50% by weight of an anionic, amphoteric or zwitterionic detergent active compound or a predominantly anionic, amphoteric or zwitterionic mixture of detergent active compounds;

provided that when the detergent active compound is an anionic detergent active compound or a mixture of anionic detergent active compounds which tends to form an insoluble calcium salt the amount of the salt of citric acid is at least 25% by weight of the composition and the amount of the anionic detergent active compound or mixture of such compounds is at least 30% by weight of the composition and the composition forms an alkaline aqueous wash solution of at least pH 9 in use at a product concentration of at least 1 gm/litre.

Suitable salts of citric acid are commercially available and include the alkali metal, ammonium and substituted ammonium salts, preferably the sodium salts. The citrates may be derived from natural or synthetic sources including for example by fermentation process. It should be appreciated that the salts of the citric acid may be formed in situ in the wash solution if desired, by incorporating citric acid and a basic material, such as sodium hydroxide, sodium carbonate or sodium silicate in the compositions. The amount of the citrate detergency builder which is used should be at least 20% by weight of the composition, preferably 25 to 40% by weight. The maximum level of the citrate builder is generally about 50%, and is dictated by practical considerations, including the cost of the sequestering agent in relation to other ingredients. When a detergent active compound is used which tends to form an insoluble calcium salt, as described below, the presence of a higher amount of a citrate builder is desirable whilst remaining within the range stated, as this tends to inhibit precipitation of the calcium salt.

In addition to the citrate detergency builder, it is possible to include minor amounts of other detergency builders, provided that the total amount of the detergency builders does not

exceed about 85% by weight so as to leave room in the composition for other essential ingredients.

Other detergency builders which can be present in minor amounts, include so-called precipitant builders which form insoluble calcium salts with the calcium present in hard water, for example sodium carbonate, sodium orthophosphate, sodium salts of long-chain alpha-sulphonated monocarboxylic acids, and alkali metal, alkyl and alkenyl succinates and malonates, and analogous compounds. Other organic or inorganic sequestrant builders can also be present in minor amounts, if desired, including for example sodium tripolyphosphate, sodium pyrophosphate, sodium nitrilotriacetate, sodium tetraacetylethylene diamine, sodium malate, sodium tartrate, trisodium carboxymethyloxysuccinate, sodium oxydiacetate, sodium hydrofuran tetracarboxylate, sodium ethane - 1 - hydroxy - 1,1 - diphosphonate, sodium oxydisuccinates and sodium mellitate, and also polyelectrolyte builders such as sodium copolyethylene maleate and sodium polyacrylate. Other water-soluble or dispersible salts of the materials may of course be used instead of the sodium salts. It will be appreciated that some of these optional additional detergency builders contain phosphorus which may detract from their usefulness in any compositions specifically intended to have a low level of phosphorus, or none at all, whilst others suffer from other deficiences such as poor biodegradability.

It is preferable to have present in the compositions an alkali metal silicate, particularly sodium silicates, for example sodium neutral silicate, alkaline silicate or metasilicate. A low level of silicate, for example about 5—10% by weight, is usually advantageous in decreasing the corrosion of metal parts in fabric washing machines. The amount and type of silicate can also be used to some extent to control the pH of wash solutions the composition, which must be alkaline, by which we mean a pH of at least 9 under the conditions of use at a product concentration of at least 1 gm/litre. The pH is preferably within the range of 9 to 11, a pH of 9 to 10 being desirable if enzymes are included in the compositions. It should, however, be noted that the high pH levels caused by high silicate levels can inhibit the action of enzymes.

If higher levels of silicate are used, for example about 10—30% by weight, there can be a noticeable improvement in detergency, particularly when the amount of silicate is about the same as that of the citrate builder, i.e. at a level of at least 20% by weight. This improvement in detergency is particularly beneficial when the compositions are used in water containing magnesium hardness, or when the detergent active compound used is one which tends to form an insoluble calcium salt, for example alkyl benzene sulphonate detergent active compounds, particularly when the lower amounts thereof are employed.

The detergent-active compounds used in the compositions of the invention may be any of the conventional anionic, nonionic, amphoteric or zwitterionic detergent-active compounds and mixtures thereof, provided that they do not form excessively water-insoluble calcium salts in hard water during use. Many such detergent-active compounds are commercially available and are fully described in the literature, for example in "Surface Active Agents and Detergents," Vols. I and II by Schwartz, Perry and Berch. Preferred detergent-active compounds which can be used include nonionic detergent-active compounds, which cannot of course form calcium salts at all, and anionic detergent-active compounds which form water-soluble calcium salts, as for example with alkyl ether sulphates, or which form insoluble calcium salts when used alone but such anionic compounds are in this case used in conjunction with additional solubilising compounds, particularly other detergent-active compounds, for example mixtures of sodium alkyl benzene sulphonates with nonionic detergent-active compounds, and some mixed olefin sulphonates, wherein some of the olefin sulphonate constituents appear to act as solubilising aids for the other less soluble constituents.

Specific nonionic detergent-active compounds which can be used in the compositions of the invention include ethoxylated fatty alcohols, preferably linear monohydric alcohols with C_{10}—C_{18}, preferably C_{10}—C_{15}, alkyl groups and about 5—15, preferably 7—12, ethylene oxide (EO) units per molecule, and ethoxylated alkylphenols with C_8—C_{16} alkyl groups preferably C_8—C_9 alkyl groups, and from about 4—12 EO units per molecule. The nonionic compounds are often used in admixture with minor amounts of other detergent-active compounds, especially anionic compounds, to improve lather characteristics and powder properties. Mixtures of nonionic compounds with amine oxides can also give good results.

The preferred anionic detergent-active compounds which form soluble or acceptable only slightly insoluble calcium salts are (C_{10}—C_{18}) alkyl sulphates and (C_{10}—C_{18}) alkyl ether (1—10 EO) sulphates, particularly the alkyl ether sulphates with C_{10}—C_{15} alkyl groups and 1 to 7 EO, and olefin sulphonate detergent-active compounds, which latter term is herein used to mean the mixture of anionic detergent-active compounds obtained when the products of the sulphonation of olefins are neutralised and hydrolysed. The olefins used are preferably linear C_{12}—C_{20} alpha-olefins, particularly C_{14}—C_{18} alpha-olefins, produced for example by the "cracked-wax" process, or by the "Zeigler" process, but localised internal, random or so-called vinylidene olefins may alter-

natively be used. The alkyl ether sulphates and olefin sulphonates are used in the form of the alkali-metal, ammonium or substituted ammonium salts, preferably the sodium salts.

Other detergent-active compounds which do not form insoluble calcium salts, but which are of less commercial interest, include salts of esters of alpha-sulphonated (C_{10}—C_{20}) fatty acids with C_1—C_{10} alcohols, preferably C_1—C_3 alcohols; salts of 2 - acyloxyalkane-1 - sulphonic acids, particularly wherein the alkyl group contains from about 10—22, preferably 12—16, carbon atoms, and the ester-forming group contains from 1—8 carbon atoms; trialkyl amine oxides having a C_{10}—C_{22} alkyl group, and two C_1—C_4 alkyl or C_2—C_3 hydroxyalkyl groups; and dialkyl sulphoxides having a C_{10}—C_{22} alkyl group and a C_1—C_3 alkyl or C_2—C_3 hydroxyalkyl group; together with detergent-active betaines and sulphobetaines.

As stated earlier, mixtures of some detergent-active compounds can give particularly good results. Specifically, alkyl benzene sulphonates, which when used alone tend to form insoluble calcium salts, and which consequently need to be used at higher levels than usual or in the presence of higher levels of the citrate detergency builder, as explained hereinafter can be used with minor amounts of solubilising compounds, such as nonionic, alkyl sulphate or alkyl ether sulphate detergent-active compounds, to give good detergent properties and be relatively economical. The amount of such solubilising detergent-active compound is preferably less than the alkyl benzene sulphonate but not less than 1 part to 10 parts by weight, especially from 1:2 to 1:8 parts, respectively.

The amount of the detergent-active compound or compounds used depends on the type of material. In the case of nonionic detergent-active compounds, or of predominantly (i.e. at least 50%) nonionic mixtures of detergent-active compounds, the amount should be at least about 15% by weight, for example from 20% to 30% by weight of the compositions, as with more than about 30% of liquid nonionic compounds there can be difficulties in producing detergent powders with satisfactory physical properties. In the case of other types of detergent-active compounds, that is to say anionic, amphoteric or zwitterionic detergent-active compounds used alone or in admixture, or in mixtures of predominantly anionic, amphoteric or zwitterionic compounds with amounts of nonionic compounds, the amount used should be at least about 25% by weight, preferably 30 to 40%, up to a maximum of about 50% of detergent-active compounds so as to leave room for other ingredients.

However, when the detergent-active compound is an anionic compound or a mixture of anionic detergent active compounds which tends to form an insoluble calcium salt the amount of the citrate builder should be at least 25% by weight of the composition and/or the amount of the detergent-active compound or compounds should be at least 30% by weight of the composition. The increased level of the builder and/or detergent active compound appears to compensate for the formation of small amounts of insoluble calcium salts of the alkyl benzene sulphonates in use when the lower levels of citrate are employed, whilst with the higher levels of citrate the free calcium level is lowered to reduce the tendency for the insoluble salts to form. Under adverse conditions of use, for example at low product concentrations in unduly hard water, it is desirable to increase the amount of both the alkyl benzene sulphonate and the citrate builder above the minimum specified levels, for example to about 30% of alkyl benzene sulphonate and 30 to 40% citrate. It is also particularly advantageous to include in such compositions relatively high levels of silicates, for example from 20% to 30% by weight.

Apart from the essential detergent-active compounds and detergency builders, the detergent compositions of the invention can contain any of the conventional optional additives in the amounts in which such additives are normally employed in fabric-washing detergent compositions. Examples of these additives include lather boosters such as alkanolamides, particularly ethanolamides derived from palm kernel fatty acids and coconut fatty acids, lather depressants, anti-redeposition agents such as sodium carboxymethylcellulose, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, peracid bleach precursors, chlorine-releasing bleaching agents such as trichlorcisocyanuric acid and alkali-metal salts of dichloroisocyanuric acid, inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluoroescent agents, colourants, perfumes, germicides and enzymes.

The presence of proteolytic enzymes in particular can make a valuable contribution to detergency with the compositions of the invention. Suitable enzymes are commercially available, often in granular form, ready for incorporating into detergent compositions; the amount of the enzyme generally being from 0.001 to 5% by weight of active enzyme, preferably 0.01 to 1% by weight of the composition, to give an activity of 5 to 20 Anson units per kilogram of the compositions. Suitable products are sold under the trade names of Alcalase, Maxatase and Protease.

The detergent compositions of the invention may be produced by any of the techniques commonly employed in the manufacture of fabric-washing detergent compositions, including particularly slurry-making and spray-drying processes, and the compositions may be

prepared in any of the common physical forms associated with fabric-washing detergent compositions, such as powders, granules, cakes and liquids.

Compositions according to the invention are further illustrated by the following Examples, in which parts and percentages are by weight, except where otherwise indicated, and water hardness is given in degrees of French hardness (°H).

EXAMPLES 1 to 8.

A series of detergent compositions were prepared with various detergent-active compounds and different levels of sodium citrate and sodium silicate, including a comparative product A based on sodium tripolyphosphate as detergency builder, as follows:

Ingredient	% in each composition								
	1	2	3	4	5	6	7	8	A
Sodium olefin sulphonate[1]	25	25	—	—	—	—	—	—	—
Sodium lauryl ether (1 EO) sulphonate	—	—	25	25	—	—	—	—	—
Nonionic detergent active compound[2]	—	—	—	—	25	25	—	—	—
Sodium alkyl benzene sulphonate[3]	—	—	—	—	—	—	25	25	18
Sodium citrate	40	20	40	20	40	20	40	40	—
Sodium tripolyphosphate	—	—	—	—	—	—	—	—	40
Alkaline sodium silicate	6	26	6	26	6	26	6	26	6
Sodium sulphate	19	19	19	19	19	19	19	—	26
Sodium carboxymethyl-cellulose	1	1	1	1	1	1	1	1	1
Water	← to 100 →								

[1] Prepared by sulphonation of an alpha-olefin (C_{14}–C_{18})

[2] Tergitol* 15–S–9, a condensation product of a secondary linear alcohol (C_{11}–C_{15}) with 9 moles of ethylene oxide

[3] Prepared by sulphonation of DOBS–055 alkyl benzene

The % detergencies of these compositions were determined using a Terg-O-Tometer with a product concentration of 0.1% in water of 18°H (Ca:Mg, 2:1) at 50°C, using a "Dacron"* polyester/cotton (65%, 35%) test cloth artificially soiled with vacuum cleaner dust. The results were as follows:

Composition	% Detergency
Example 1	50.2
Example 2	48.3
Example 3	52.8
Example 4	50.7
Example 5	44.0
Example 6	44.3
Example 7	43.3
Example 8	52.0
Product A	49.0

*(Trade Mark.)

These results indicate some superiority for the compositions based on sodium olefin sulphonate and sodium lauryl ether sulphate detergent-active compounds, and near equivalence for the nonionic-based compositions of Examples 5 and 6, and for the low silicate composition of Example 7 with sodium alkyl benzene sulphonate, against the comparative sodium tripolyphosphate-built product A. It will be noted that by increasing the level of silicate in the compositions when the level of sodium citrate is decreased in Examples 2, 4 and 6, the percentage detergency is hardly affected, whilst with Example 8 the increased level of silicate at the continued high citrate level boosts detergency sufficiently under the test conditions employed. When the composi-

tions of Examples 7 and 8 were tested for detergency at 0.15% product concentration they were found to have percentage detergencies of 52.9 and 62.4%, respectively, as against a detergency of 54.6% for the comparative product A under the same test conditions.

EXAMPLES 9 to 11.

Three compositions were prepared to the formulation below:

Ingredient	%
Detergent active compound[1]	48
Sodium citrate	20
Alkaline sodium silicate	20
Sodium metasilicate	6
Sodium carboxymethylcellulose	1
Water	5

[1] In Example 9, sodium olefin sulphonate
In Example 10, sodium lauryl ether (1 EO) sulphate
In Example 11, sodium alkyl benzene sulphonate

The percentage detergencies of these products were determined by the procedure described for Examples 1 to 8, with the following results, including a result for the comparative product A described above.

Product	% Detergency
Example 9	54.6
Example 10	57.7
Example 11	51.4
Product A	43.8

These results show significantly improved results for the compositions of the invention. It should be noted that the different result for the detergency of product A, compared with Examples 1 to 8 is caused by a different batch of test cloth.

EXAMPLES 12 and 13.

Three detergent powders were prepared to the following formulations, including one comparative product B, of conventional sodium tripolyphosphate-built type:

Ingredient	% in Product		
	Example 12	Example 13	Product B
Sodium olefin sulphonate[1]	25.5	—	—
Nonionic detergent active compound[2]	—	25.5	—
Sodium alkyl benzene sulphonate[3]	—	—	17.5
Sodium citrate	40	40	—
Sodium tripolyphosphate	—	—	40
Alkaline sodium silicate	—	—	6
Sodium metasilicate	6	6	—
Sodium sulphate	15.5	15.5	23.5
Sodium carboxymethylcellulose	1	1	1
Water	to 100	to 100	to 100

[1] Prepared by the sulphonation of a Zeigler alpha-olefin (C_{14}:C_{16}:C_{18}, 40:40:20)

[2] Tergitol 15—S—9, a condensation product of secondary linear alkyl (C_{10}—C_{15}) alcohol with 9 moles of ethylene oxide

[3] Prepared by sulphonation of DOBS—055 alkyl benzene

The products were compared in practical washing tests in Whirlpool washing machines using 18°H water (Ca:Mg, 2:1) at 45°C and 0.15% product concentration, to wash domestically soiled cotton towels, tea towels and pillowcases. The results showed there to be a very slight preference for the products washed using Examples 12 and 13 over product B.

EXAMPLE 14.

A detergent composition was prepared to the following formulation:

Ingredient	%
Sodium olefin (C_{15}—C_{18}) sulphonate[1]	25.0
Sodium citrate	20.0
Alkaline sodium silicate	20.0
Sodium metasilicate	6.0
Sodium sulphate	17.5
Fluorescent agent	0.5
Sodium carboxymethylcellulose	1.0
Water	10.0

[1] Prepared by sulphonation of a C_{15}—C_{18} cracked wax olefin

This product was compared in practical washing tests with a comparative product C, in which the sodium olefin sulphonate was replaced by sodium alkyl benzene sulphonate, and with comparative product B, as described above, but also containing 0.5% of the fluorescent agent. The tests were performed as described for Examples 12 and 13 except that the product concentration used was 0.1%. The results showed the product of Example 14 to be marginally better than the sodium tripolyphosphate-based product B, with the product C having a much less satisfactory performance.

EXAMPLES 15 to 54.

A series of detergent compositions were prepared to the formulations shown in Table I below, using in each case, one of four basic formulations and one of nine detergent active compounds or mixtures thereof.

The detergencies of these compositions were determined in a Terg-O-Tometer using standard test conditions with water of either 9°H or 18°H Ca^{2+}:Mg^{2+}, 2:1) at 50°C, and pH 10, using a product concentration of 0.1%. Washing was conducted for 10 minutes at 90 cycles/minute followed by a 2 minute rinse, and a "Dacron" polyester/cotton (65:35) test cloth soiled with vacuum cleaner dust was used. The detergency tests results are also shown in Table I.

TABLE I

Ingredient	% in the formulations			
	Examples 15—23	Examples 24—32	Examples 33—41	Examples 42—50
Detergent active compound(s)	25	25	40	40
Sodium citrate	25	40	25	40
Sodium alkaline silicate	6	6	6	6
Sodium sulphate	34	19	19	4
SCMC	1	1	1	1
Water	9	9	9	9

The detergent active compounds used and the detergency test results were as follows:

TABLE I (Continued)

Examples	Compound(s)	% Detergency for Examples			
		Ex 15–23	Ex 24–32	Ex 33–41	Ex 42–50
		9°H / 18°H	9°H / 18°H	9°H / 18°H	9°H / 18°H
15, 24, 33, 42	alkyl benzene sulphonate[1]	62.2, 30.4	68.7, 47.6	64.9, 41.8	68.9, 58.8
16, 25, 34, 43	4:1 parts of alkyl benzene sulphonate and nonionic compound[2]	62.0, 39.4	68.6, 47.9	62.9, 45.8	–, 57.5
17, 26, 35, 44	4:1 parts of alkyl benzene sulphonate and alkyl ether sulphate[3]	62.8, 46.0	69.9, 50.1	64.5, 51.8	–, 60.3
18, 27, 36, 45	alkyl sulphate[4]	64.6, 49.9	70.3, 54.4	66.9, 54.3	–, 61.3
19, 28, 37, 46	olefin sulphonate[5]	57.2, 45.0	64.3, 47.1	59.6, 48.7	–, 56.0
20, 29, 38, 47	alkyl ether sulphate[6]	52.3, 46.3	57.3, 53.0	59.0, 52.5	52.3, 58.8
21, 30, 39, 48	sulphobetaine[7]	57.8, 49.8	63.5, 56.8	61.5, 52.8	57.8, 57.8
22, 31, 40, 49	amine oxide[8]	58.6, 52.3	63.6, 55.8	59.4, 52.9	58.6, 55.1
23, 32, 41, 50	nonionic compound[9]	51.6, 45.1	61.2, 48.8	56.5, 47.8	51.6, 53.8

[1] Sodium secondary linear alkyl (C_{11}–C_{15}) benzene sulphonate obtained from Monsanto Alkylate 230
[2] 4 parts of the alkyl benzene sulphonate as in [1] above to 1 part of secondary alcohol (C_{11}–C_{15}) – 9 EO condensate obtained as Tergitol 15–S–9
[3] 4 parts of the alkyl benzene sulphonate as in [1] above to 1 part of sodium primary alcohol (C_{12}–C_{15}) – 3 EO sulphate obtained from Dobanol 25
[4] Sodium primary alcohol (C_{14}–C_{15}) sulphate, obtained from Dobanol 45
[5] Sodium olefin sulphonate prepared from Zeigler α-olefin (C_{14}:C_{16}:C_{18}, 40:40:20)
[6] Sodium lauryl alcohol – 1 EO sulphate
[7] Hexadecyldimethylammoniopropane sulphonate
[8] N,N-dimethylcocoamine oxide
[9] Secondary-alcohol (C_{11}–C_{15}) – 9 EO condensate

Two conventional control formulations were also prepared as follows:

Ingredient	% D	% E
Alkyl benzene sulphate	18	—
Nonionic compound	—	18
Sodium tripolyphosphate	40	40
Sodium alkaline silicate	6	6
Sodium sulphate	26	26
SCMC	1	1
Water	9	9

By way of comparison, the % detergency of the control formulation D under the same conditions was 69.4% (at 9°H) and 52.5% (at 18°H), and for control formulation E the % detergency was 65.0% (at 9°H) and 50.3% (at 18°H).

These results show several of the preferred compositions to be generally equivalent in performance to the sodium tripolyphosphate-based control product. With alkyl benzene sulphonate as the sole detergent active compound a poor result was obtained at low levels of the detergent active compound and the citrate builder in 18°H water (i.e. an under-built situation).

EXAMPLES 51 to 77.

A further series of detergent compositions were prepared to one of three basic formulations each containing a high level of sodium alkaline silicate. The detergent active compounds were varied as with Examples 15 to 54, and each composition had one of ten detergent active compounds or a mixture thereof. The compositions were tested for detergency using the procedure described for Examples 15 to 54, except that only 18°H water was used, and the formulations and detergency test results are shown in Table II below.

TABLE II

Ingredient	% in the formulation Examples 51–59	Examples 60–68	Examples 69–77
Detergent active compound	25	25	40
Sodium citrate	25	25	25
Sodium alkaline silicate	26	45	26
Sodium sulphate	14	—	—
SCMC	1	1	1
Water	9	4	9

Examples	Detergent compound(s)[1]	% detergency (18°H)		
51, 60, 69	alkyl benzene sulphonate	50.9	61.9	58.5
52, 61, 70	4:1 parts alkyl benzene sulphonate and nonionic compound	49.6	60.0	60.8
53, 62, 71	4:1 parts of alkyl benzene sulphonate and alkyl ether sulphate	54.2	62.0	63.0
54, 63, 72	alkyl sulphate	56.9	62.9	65.5
55, 64, 73	olefin sulphonate	51.6	57.2	58.9
56, 65, 74	alkyl ether sulphate	52.1	59.1	57.1
57, 66, 75	sulphobetaine	57.1	61.2	57.7
58, 67, 76	amine oxide	56.9	62.9	56.6
59, 68, 77	nonionic compound	47.3	51.8	53.5

[1] The detergent compounds used were the same as in Examples 15–50 respectively

Comparison of these results with those of Examples 15—50 shows substantial benefits for the increased silicate levels, particularly with the compositions containing lower levels of detergent active compound and citrate. Over all conditions, the best detergent active compound was the alkyl sulphate of Examples 18, 27, 36, 45, 54, 63 and 72. The alkyl benzene sulphonate with additional nonionic or alkyl ether sulphate detergent compound was generally superior to the alkyl benzene sulphonate in underbuilt conditions and at least as good under optimum overbuilt conditions. It was also noticeable that the olefin sulphonate was generally fairly good, and superior to the alkyl benzene sulphonate alone under adverse underbuilt conditions.

EXAMPLES 78 to 80.

Three detergent compositions according to the invention and two comparative products F and G were prepared to the following formulations:

Ingredient	%				
	Ex 78	Ex 79	Ex 80	Product F	Product G
Sodium secondary linear alkyl (C_{11}–C_{15}) benzene sulphonate	30	30	30	16	16
Trisodium citrate	25	40	40	40	—
Sodium tripolyphosphate	—	—	—	—	40
Sodium alkaline silicate	45	10	30	10	10
Water	← to 100 →				

These compositions were compared for performance in washing domestically-soiled halved articles and artificially-soiled test cloths using RCA Whirlpool automatic washing machines with an 8lb load in 14 gallons of water and a wash temperature of 48°C and a wash cycle of 14 minutes. Each washing was carried out under a variety of conditions as regards product concentration and water hardness. The washed articles were compared in triplicate for appearance against those washed with the control product G in each case, to give the overall test results in terms of the visual preference for the washed articles as shown in Table III.

Ingredient	%		
	Example 81	Example 82	Example 83
Sodium secondary linear alkyl (C_{11}–C_{15}) benzene sulphonate	20	20	30
Secondary alcohol (C_{12}–C_{15}) – 9 EO	5	5	—
Sodium citrate	25	25	40
Sodium alkaline silicate	6	—	10
Sodium neutral silicate	—	40	—
Enzyme ("Alcalase") noodles	1	1	1
Water	← to 100 →		

These results show that under a variety of conditions compositions can be made according to the invention which are generally equivalent in practical performance to a conventional sodium tripolyphosphate-built product, especially when the compositions have a high citrate and high silicate content. It will be noted that the fabrics washed with product F, having an inadequate level of alkyl benzene sulphonate, were very inferior to that washed with the conventional sodium tripolyphosphate product.

EXAMPLES 81 to 83.

Three detergent compositions were prepared with the following formulations:

TABLE III

Product Concentration	Water Hardness	Product paired comparisons against Product G			
		Example 78	Example 79	Example 80	Product F
0.1	8°H (Ca:Mg, 3:1)	Comparable	–	Comparable	–
0.15	8°H (Ca:Mg, 3:1)	Slightly inferior	Comparable	Comparable	–
0.3	8°H (Ca:Mg, 3:1)	–	–	Slightly inferior	–
0.15	9°H (Ca:Mg, 2:1)	–	Comparable	–	Very inferior
0.1	18°H (Ca:Mg, 2:1)	Comparable	Comparable	Preferred	–
0.2	18°H (Ca:Mg, 2:1)	Comparable	Comparable	Slight preference	–
0.3	18°H (Ca:Mg, 2:1)	Slightly inferior	Comparable	Comparable	–

These compositions were compared for detergency in an RCA Whirlpool washing machine with domestically-soiled cotton towels, tea towels and pillowcases using a product concentration of 0.15% in water of 18°H (Ca:Mg, 2:1) at 50°C. The wash solutions had initial pHs of about 9.0, 9.5 and 9.0 respectively. It was found that the product of Example 82 had a better performance than that of Example 81, which was in turn generally equivalent in performance to a comparative commercially available sodium tripolyphosphate product without enzymes, whilst Example 83 was generally equivalent to a similar comparative product containing enzymes.

WHAT WE CLAIM IS:—

1. A detergent composition comprising at least 20% by weight of a salt of citric acid detergency builder and either

(a) at least 15% by weight of a nonionic detergent active compound or a predominantly nonionic mixture of detergent active compounds; or

(b) from 25% to 50% by weight of an anionic, amphoteric or zwitterionic detergent active compound or a predominantly anionic, amphoteric or zwitterionic mixture of detergent active compounds;

provided that when the detergent active compound is an anionic detergent active compounds or a mixture of anionic detergent active compounds which tends to form an insoluble calcium salt the amount of the salt of citric acid is at least 25% by weight of the composition and the amount of the anionic detergent active compound or mixture of such compounds is at least 30% by weight of the composition, and the composition forms an alkaline aqueous wash solution of at least pH 9 in use at a product concentration of at least 1 gm/litre.

2. A detergent composition according to claim 1, wherein the salt of citric acid is sodium citrate.

3. A detergent composition according to claim 1 or claim 2, wherein the amount of the salt of citric acid is from 25 to 40% by weight of the composition.

4. A detergent composition according to any of the preceding claims, comprising from 15% to 30% by weight of a nonionic detergent active compound or a mixture of predominantly nonionic detergent active compounds.

5. A detergent composition according to any of claims 1 to 3, comprising from 25% to 40% by weight of an alkyl sulphate, alkyl ether sulphate or olefin sulphonate detergent active compound.

6. A detergent composition according to any of claims 1 to 3, comprising from 25% to 40% of a mixture of alkyl benzene sulphonate detergent active compound and a minor amount of a solubilising nonionic, alkyl sulphate or alkyl ether sulphate detergent active compound.

7. A detergent composition according to any of claims 1 to 3, comprising an alkyl benzene sulphonate detergent active compound, the amount of the citrate detergency builder being at least 25% by weight of the composition and the amount of the alkyl benzene sulphonate being at least 30% by weight of the composition.

8. A detergent composition according to any of the preceding claims, additionally comprising at least 20% by weight of sodium alkaline silicate, neutral silicate or metasilicate.

9. A detergent composition according to any of the preceding claims, additionally comprising from 0.01 to 1% by weight of a proteolytic enzyme.

10. A detergent composition acording to claim 1 substantially as described herein with reference to any of the Examples.

R. V. TATE,
Chartered Patent Agent,
Unilever Limited,
Unilever House,
London E.C.4.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1975.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.